

PATENT SPECIFICATION

NO DRAWINGS

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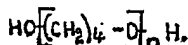
COMPLETE SPECIFICATION

Improvements in or relating to Thermally Stable Block Copolymers of Formaldehyde

We, INSTITUT KHIMICHESKOI FIZIKI AN USSR, of Vorobievskoe Shosse 2b, Moscow, Union of Soviet Socialist Republics (USSR), a Body Corporate organised under the laws of the USSR, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 THIS INVENTION relates to a method of preparing a thermally stable block copolymer of formaldehyde and, more particularly it relates to processes of preparing a thermally stable block copolymer by the polymerization of formaldehyde under the action of ionic catalysts in the presence of a polyether or polyacetal.

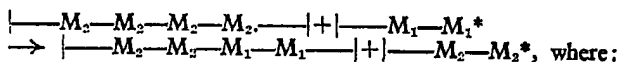
20 Known in the art is a method of preparing block copolymers of formaldehyde by the polymerization of formaldehyde in an inert organic medium under the action of ionic catalysts in the presence of heterogeneous-chain polymers, having active hydrogen atoms at the ends of macromolecules, e.g. in the presence of polytetramethylene glycol



However, the block copolymers prepared by the prior art procedure have low thermal stabilities owing to the presence of end blocks of polyoxymethylene glycols. Improvement of the thermal stabilities of such block copolymers calls for acetylation so as to block the terminal hydroxyl groups. The acetylation step makes the process of manufacturing such block copolymers much more elaborate and expensive, since it involves the employment of large quantities of acetylating agents e.g. acetic anhydride) and solvents, and also calls for complicated techniques of washing the block copolymers.

It has now been found that thermally stable block copolymers free from the above-mentioned disadvantages may be prepared, if the heterochain polymer used is a polyether or polyacetal which contains no active hydrogen atoms at the ends of their macromolecules; an example is polydioxolane.

In this case, the polyethers or polyacetals participate in chain transfer with simultaneous chain rupture, according to the following reaction scheme:



55 $|-\text{M}_2-\text{M}_2-\text{M}_2-\text{M}_2-|$ is a homopolymer of M_2 monomer, e.g., dioxolane;

$|-\text{M}_1-\text{M}_1^*$ is a growing active macromolecule of M_1 monomer (i.e. formaldehyde);

60 $|-\text{M}_2-\text{M}_2-\text{M}_1-\text{M}_1-|$ is a block co-

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polymer of M_1 and M_2 monomers; and

$|-\text{M}_2-\text{M}_2^*$ is a growing active macromolecule of M_2 monomer.

The occurrence of a large number of elementary processes of chain transfer with simultaneous chain rupture shown in the above

reaction scheme results in the formation of alternating block copolymers of formaldehyde and polyethers or polyacetals; such block copolymers have a regular structure and are noted for their high thermal stability.

Thus, the present invention consists in a method of preparing a formaldehyde block copolymer by the polymerization of formaldehyde and a polyether or polyacetal (as hereinafter defined) in an inert inert organic medium and in the presence of an ionic catalyst.

The terms "polyether" and "polyacetal" as used herein are defined to mean a polymer of a cyclic ether or a polymer having the structure of a polymer of a cyclic ether, and a polymer of a cyclic acetal or a polymer having the structure of a polymer of a cyclic acetal, respectively, said polymers having no active hydrogen atoms at the ends of their macromolecules. A number of methods of preparing such polymers are known and are described for example, by: P. H. Pleash & I. H. Westermann, *Materials of International Symposium of Macromol. Chem.*, Prague (1965); Jaacks V. *Macromol. Chem.* 99, 300, (1966); and H. Kämmerer & P. N. Grover, *Makromolek. Chem.* 96 (1966), 270—282.

It is preferred that the polyether or polyacetal employed is polydioxolane or an ethylene oxide homopolymer or propylene oxide homopolymer.

The molecular weight of the polyether or polyacetal used may be high or low, but the employment of higher molecular weight polyethers or polyacetals is more advantageous as it increases the probability of chain transfer with chain rupture, whereas a marked improvement in thermal stability of block copolymers is attained with low concentrations of primary polymers (polyethers or polyacetals).

In accordance with the present invention, the polyether or polyacetal may be employed in an amount that provides up to 50% by weight of said polyether or polyacetal in the resultant block copolymer.

However, the preferred amount of the polyether or polyacetal is less than 5% by weight.

According to the present invention, the polymerization catalysts used are cationic or anionic catalysts suitably selected from the group of compounds known as Lewis acids, viz., boron, aluminum, iron, antimony, zinc, tin, and titanium halides; complex compounds of said halides with electron-donating organic compounds that contain oxygen nitrogen or sulphur atoms; strong mineral acids, diazonium salts of Lewis acids; and amines, quaternary ammonium bases and salts thereof.

In a preferred embodiment of the present invention, use is made of such catalysts as metal halides, particularly tin tetrachloride.

The quantity of catalysts may vary from 1×10^{-1} to 1×10^{-3} mole per litre of reaction mass, the preferred catalyst concentration ranging from 1×10^{-3} to 1×10^{-2} mole/litre.

The polymerization reaction may be carried out at a temperature of 0 to 100°C, preferably from 25 to 70°C.

Inert organic media for the polymerization reaction include all organic media capable or incapable of dissolving the monomer and/or block copolymer and selected from the group of aliphatic, cycloaliphatic or aromatic hydrocarbons and halogen or nitro derivatives thereof.

The following media are useful for the present method; cyclohexane, benzene, toluene, heptane, octane, pentane, ligroin, petroleum ether, carbon tetrachloride, methylene chloride, nitrobenzene nitromethane, or mixtures thereof.

In order to remove the non-stable portion of block copolymers said non-stable portion being composed of terminal blocks of polyoxymethylene glycols or formaldehyde, homopolymers, the block copolymers obtained by the polymerization reaction may be subjected to alkaline treatment.

Said treatment is preferably effected with heating in an aqueous medium or in a medium of organic solvents, the alkaline agents employed being alkalis, ammonia, or primary amines.

The thermal stability of block copolymers thus prepared is evaluated by determining the degree (percentage) of block copolymer decomposition when said block copolymers are heated in vacuo at 220°C for a period of 30 minutes.

The following kinetic technique is useful for ascertaining that the products prepared by the present method are actually the desired block copolymers and are not a mixture of homopolymers. When the block copolymer is heated to a temperature in excess of the decomposition temperature of one of the homopolymers, there occurs chain depolymerization of macromolecules, and this process will proceed until it reaches the block of the other polymer, whose decomposition temperature is higher than that of the first one. Where the material under test comprises a mixture of two homopolymers, the macromolecules of the first homopolymer will be decomposed completely, so that only the macromolecules of the second homopolymer remain. Correlation between the portion of the polymerization product that was been decomposed, and the quantity of the first monomer used in the polymerization reaction makes it possible to decide unequivocally, whether the polymerization product in question is a block copolymer or a mixture of two homopolymers.

The block copolymers obtained by the process of the present invention lend themselves

to processing into high quality plastics in the presence or absence of various conventional thermal stabilizers, antioxidants, plasticizers, fillers, and pigments, etc.

- 5 The following examples are presented by way of illustration. The polyethers and poly acetals used are all free from active terminal hydrogen atoms on the macromolecules and were prepared by one of the known methods.

10

EXAMPLE 1

Formaldehyde gas, obtained by pyrolysis of 50 g of alpha-polyoxymethylene, was passed successively through two coils maintained at a temperature of -15 to -16°C .

- 15 Next formaldehyde gas was passed through a column packed with aluminosilicate and cooled to a temperature of -18 to -16°C .

The monomeric formaldehyde gas thus obtained contained less than 0.1% of impurities; it was fed continuously into a reactor containing 20 ml of toluene in which the catalyst, SnCl_4 , was dissolved in an amount sufficient to obtain the catalyst concentration of 2.87×10^{-3} mole/litre and polydioxolane (MW 2,000) in a concentration of 2% by weight. The polymerization was carried out at room temperature for 40 minutes and was then terminated by adding methanol to the reaction mixture.

- 30 The suspension of the block copolymer thus obtained was filtered off. The block copolymer on the filter was washed with methanol and ether, and dried in a vacuum drying cabinet at 60°C to constant weight.

35 The weight of the dry block copolymer obtained was 5.8 g.

With a view to eliminating the non-stable portion, the block copolymer was treated with boiling aqueous sodium hydroxide (concentration, 10% by weight). The block copolymer was then washed with hot water until the reaction of the washings was neutral and dried in a vacuum drying cabinet at 60°C to constant weight.

45 The weight of the dry block copolymer was 4.45 g (77.0% by weight of the block copolymer prior to alkaline treatment).

The molecular weight of the block copolymer, obtained by the procedure disclosed in this and subsequent examples, was evaluated on the basis of intrinsic viscosity data determined at 150°C on block copolymer solutions in dimethylformamide containing 2% of diphenylamine.

55 The intrinsic viscosity of the block copolymer of the present example is $[\eta] = 0.4$.

In a parallel blank test, formaldehyde is subjected to polymerization under the conditions disclosed hereinabove, except that no polydioxolane is added and the polymer obtained is not treated with boiling alkaline solution.

60 Here and in both the subsequent Examples, as well as in the blank test, the thermal

stability of the polymers was evaluated by determining the degree (percentage) of decomposition of the polymer subjected to heating at 220°C for 30 minutes under vacuum.

In the block copolymer of the present example, the degree of decomposition equalled 1.0%.

The formaldehyde homopolymer prepared in the blank test underwent decomposition to the extent of 67%.

EXAMPLE 2

The procedure was similar to that disclosed in Example 1, except that ethylene oxide homopolymer (MW, 140,000) was used in place of polydioxolane.

The block copolymer thus obtained underwent decomposition to the extent of 4.8%.

EXAMPLE 3

The procedure was similar to that disclosed in Example 1, except that propylene oxide homopolymer was used in place of polydioxolane.

The degree of decomposition of the block copolymer obtained was 3.5%.

WHAT WE CLAIM IS:—

1. A method of preparing a formaldehyde block copolymer by the polymerisation of formaldehyde and a polyether of polyacetal (as hereinbefore defined) in an inert organic medium and in the presence of an ionic catalyst.

2. A method according to claim 1, in which the said polymerisation is effected at a temperature of from 0 to 100°C .

3. A method according to claim 2, in which the said polymerisation is effected at a temperature of from 25 to 70°C .

4. A method according to any one of claims 1, 2 and 3, in which the said polyether is ethylene oxide homopolymer.

5. A method according to any one of claims 1, 2 and 3, in which the said polyether is propylene oxide homopolymer.

6. A method according to any one of claims 1, 2 and 3, in which the said polyacetal is polydioxolane.

7. A method according to any one of claims 1 to 6, in which the amount of said polyether or said polyacetal incorporated is less than 50% by weight of the resultant block copolymer.

8. A method according to claim 7, in which the said amount is less than 5% by weight of the resultant block copolymer.

9. A method according to any one of claims 1 to 8, in which the said ionic catalyst is a Lewis acid.

10. A method according to any one of claims 1 to 8, in which the said ionic catalyst is a complex compound of a Lewis acid with an electron-donating compound containing an oxygen, nitrogen or sulphur atom.

11. A method according to claim 9 or claim 10, in which the said Lewis acid is a metal halide.
12. A method according to claim 11, in which said metal halide is tin tetrachloride.
13. A method according to any one of claims 1 to 8, in which the said ionic catalyst is a strong mineral acid.
14. A method according to any one of claims 1 to 8, in which the said ionic catalyst is a diazonium salt of a Lewis acid.
15. A method according to any one of claims 9 to 14, in which the concentration of said ionic catalyst is from 10^{-4} to 10^{-1} mole/litre of reaction mass.
16. A method according to claim 15, in which the said concentration is from 10^{-3} to 10^{-2} mole/litre of reaction mass.
17. A method according to any one of the preceding claims, in which the said inert organic medium is toluene.
18. A method according to claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.
19. A formaldehyde block copolymer when prepared by the method of any one of the preceding claims.

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